OVERVIEW OF COAL ASH DEPOSITION IN BOILERS

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INTRODUCTION

The management of coal ash in utility boilers continues to be one of the most important fuel property considerations in the design and operation of commercial boilers. The behavior of mineral matter in coal can significantly influence furnace sizing, heat transfer surface placement, and convection pass tube spacing. Ironically, many of the more reactive, low rank U. S. coals must have larger furnaces than the less reactive higher rank coals. This is strictly a requirement based on the mineral matter behavior; Figure 1 illustrates this point. Given the same mineral matter behavior the more reactive, lower rank coals would require less residence time and therefore smaller furnace volumes than the less reactive, higher rank coals.

Although pulverized coal has been fired for more than 50 years and much is known about combustion behavior there are still a number of boilers experiencing operational problems from coal ash effects. Ash-related problems are one of the primary causes of unscheduled outages, unit derating and unavailability. Because of variability in a given coal seam and since many boiler operators may experience changes in their coal supply during the life of a boiler, operational problems caused by changes in coal ash properties can significantly affect boiler performance. Not only must the initial boiler design be correctly determined based on the specification coal but reliable judgements must be made regarding the suitability of other candidate coals and their effect on operation during the lifetime of the boiler.

The increased emphasis on coal usage in this country and, indeed, the significant effort underway to consider coal water mixtures as possible oil substitutes in oil-designed boilers underscores the need to improve the prediction of mineral matter behavior in a boiler environment.

Coal is a very heterogeneous, complex material which produces heterogeneous, complex products during combustion. Since, during pulverized coal combustion, coal particles of various organic and mineral matter compositions can behave in completely different manners, prediction based upon the overall or average composition may be misleading. Like many of the currently-used ASTM coal analyses, the method for determining ash fusibility temperatures was developed when stoker firing was a predominant coal firing technique; the methodologies and conditions employed during many of the ASTM tests reflect this. It is not surprising that the usefulness of some ASTM test results may be limited when used for a pulverized coal firing application. In recent years researchers have developed methodologies for characterizing coal ash behavior that better reflect the fundamental mechanisms controlling behavior and more closely simulate the conditions that exist in a pulverized coal fired boiler.

Clearly there is a need for improved mineral matter behavior predictive techniques. This paper will provide a statement of the ash deposition problem in pulverized coal fired boilers, it will present an assessment of the older, traditional methods for predicting mineral matter behavior and it will address some of the newer techniques that have been suggested as better ways of characterizing coal ash behavior. Additionally some areas of uncertainty will be identified as requiring the development of better predictive techniques.

STATEMENT OF THE PROBLEM

The presence of ash deposits and flyash can create the following problems in a boiler:

1. Reduced heat transfer
2. Impedance of gas flow
3. Physical damage to pressure parts
4. Corrosion of pressure parts
5. Erosion of pressure parts

These problems can result in reduced generating capacity, unscheduled outages, reduced availability, and costly modifications.

Ash which deposits on boiler walls in the radiant section of a furnace is generally referred to as slagging. Ash deposition on convection tube sections downstream of the furnace radiant zone is typically referred to as fouling. Ash slagging and fouling can result in problems listed in items 1 through 4; item 5, erosion, is the result of impingement of abrasive ash on pressure parts. Often coal ash deposit effects are inter-related. For example, slagging will restrict waterwall heat absorption changing the temperature distribution in the boiler which in turn influences the nature and quantity of ash deposition in downstream convective sections. Ash deposits accumulated on convection tubes can reduce the cross-sectional flow area increasing fan requirements and also creating higher local gas velocities which accelerates flyash erosion. In situ deposit reactions can produce liquid phase components which are instrumental in tube corrosion.

One of the most common manifestations of a deposition problem is reduced heat transfer in the radiant zone of a furnace. Decreased heat transfer due to a reduction in surface absorptivity is a result of the combination of radiative properties of the deposit (emissivity/absorptivity) and thermal resistance (conductivity) of a deposit. Thermal resistance (thermal conductivity and deposit overall thickness) is usually more significant because of its effect on absorbing surface temperature.

Previous work has indicated that the physical state of the deposit can have a significant effect on the radiative properties, specifically molten deposits show higher emissivities/absorptivities than sintered or powdery deposits (Ref. 1). Although thin, molten deposits are less troublesome from a heat transfer aspect than thick, sintered deposits, molten deposits are usually more difficult to remove and cause frozen deposits to collect in the lower reaches of the furnace; physical removal then becomes a problem for the wall blowers.

Impedance to gas flow is the result of heavy fouling on tubes in the convective section. Problems of this type are most likely to occur with coals having high sodium contents, usually found in low rank coal deposits in Western U.S. seams. Hard, bonded deposits can occur which are resistant to removal by the retract soot-blowers.

Physical damage to pressure parts can occur if large deposits have accumulated in the upper furnace and proceed to become dislodged or blown off and drop onto the slopes of the lower furnace. Such deposits are usually characterized by their relatively high bonding strengths and their heavily sintered structure.

Fireside corrosion can occur on both waterwall and superheater tube surfaces. Normal sulfates and pyrosulfates are frequently the cause of waterwall corrosion, although reducing conditions can also cause depletion of protective oxide coatings on tube surfaces. On higher temperature metal surfaces, (superheaters/reheaters) alkali-iron-trisulfates are often the cause of corrosion. Chlorine can also be a contributing factor toward superheater metal corrosion. While exact mechanisms can be argued there have been examples of both liquid phase and gas phase corrosion when chlorides have been present (Ref. 2).

Erosion of convective pass tubes, while not a function of deposits, is caused by the abrasive components in flyash. Flyash size and shape, ash particle composition and concentration, and local gas velocities play important roles concerning erosion phenomenon. Recent work has shown that quartz particles above a certain particle size are very influential in the erosion process and that furnace temperature history plays an important role in determining erosive characteristics of the particles (Ref. 3 & 4).

FUNDAMENTAL CONSIDERATIONS IN ASH DEPOSITION

The coal ash deposition process is extremely complex and involves numerous aspects of coal combustion and mineral transformation/reaction. The following all play a role in the formation of ash and the depositon process.

- Coal Organic Properties
- Coal Mineral Matter Properties
- Combustion Kinetics
- Mineral Transformation and Decomposition
- Fluid Dynamics
- Ash Transport Phenomena
- Vaporization and Condensation of Ash Species
- Deposit Chemistry - Specie Migration and Reaction
- Heat Transfer To and From the Deposit

Despite considerable research in these areas, there are many gaps in our fundamental understanding of the mechanisms responsible for mineral matter behavior. Although substantial knowledge exists concerning the deposition process, the complexity of the subject does not allow detailed discussion here. However, the importance of furnace operating conditions on the combined results of each of the above areas must be stressed. For a given coal composition, furnace temperatures and residence times generally dictate the physical and chemical transformations which occur. The ash formation process is primarily dependent on the time/temperature history of the coal particle. The resultant physical properties of a given ash particle generally determine whether it will adhere to heat transfer surfaces. Local stoichiometries can also influence the transformation process and thereby the physical characteristics of ash particles; iron-bearing particles are a prime example of this.

Aerodynamics can play a role in the ash deposition process in all furnaces regardless of the type of firing; recent interest in microfine grinding of coal is testimony to this fact. It has been postulated that smaller ash particles will follow gas streamlines and be less likely to strike heat transfer surfaces. This is a logical hypothesis for those ash particles that cause deposition due to an impact mechanism. In addition to particle size, particle density and shape also affect aerodynamic behavior. Molten, spherical particles will be less likely to follow gas streamlines than angular or irregular particles of the same mass due to the difference in drag forces.

Most coal ash will result in deposits of increasing severity with increasing gas temperature. This is not a linear relationship, as illustrated in Figure 2, but rather shows a progressively more severe ash deposit condition with increasing gas temperature (Ref. 5). Boilers are normally designed so that cleanable, sintered deposits will be formed. This is a reasonable compromise between a very large, economically uncompetitive boiler that may produce very dry, dusty deposits and a very small, highly loaded boiler that would produce molten, running ash deposits.

The key governing factor, then, is determining how small a furnace can be, for a given MW output, and still result in deposits that are cleanable with conventional sootblowing equipment.

Because of the complexity of the ash formation and ash deposition process, it seems logical to deal first with those key coal constituents most responsible for ash deposition. The iron and sodium contents of an ash have typically been considered key constituents. Techniques have been developed to determine how these key constituents are contained in the coal, i.e., the particular mineral forms that are present or the grain size of the constituent in question. Obviously the remainder of the mineral matter has an effect, but depending on the concentration and form in which iron and/or sodium constituents are present, the remaining mineral matter often has second order effects.

As previously discussed, ash formation and the resulting ash size distribution is extremely complex and is dependent on several factors including initial coal size, coal burning characteristics, mineral content, mineral grain size, volatile ash species, melting behavior of the mineral matter, and temperature history of the particle. Generally, coal containing lower melting mineral matter has a greater potential for ash agglomeration as the particle burns and yields fewer ash particles per coal particle which results in coarser ash particles than those of coal with higher melting ash. Obviously things like ash quantity, and mineral grain sizes could influence this hypothesis. The way a coal particle burns may also influence the number of ash particles generated, i.e., a shrinking sphere burning mode may produce a different result from a constant diameter, decreasing density mode of burning; swelling coals may behave differently than non-swelling coals.

In reflecting on the above discussion, it becomes apparent that one cannot completely divorce the predictive techniques employed, from the particular coal burning application. Pulverized coal firing will require a sensitivity to different conditions than stoker firing, or a slagging combustor. Failure to address the specific conditions inherent in each type of firing system will lead to lower resolution in one's predictive abilities than desired.

ASSESSMENT OF TRADITIONAL PREDICTIVE METHODS

ASTM measurements such as ash fusibility (D1857) have formed the basis for traditional ash behavior predictive techniques. These bench-scale tests provide relative information on a fuel; this is used in a comparative fashion with similar data on fuels of known behavior. Unfortunately, the commonly used tests do not always provide sufficient information to permit accurate comparison.

The fusibility temperature measurement technique attempts to recognize the fact that mineral matter is made up of a mixture of compounds each having their own melting point. As a cone of ash is heated some of the compounds melt before others and a mixture of melted and unmelted material results. The structural integrity or deformation of the traditional ash cone changes with increasing temperature as more

of the minerals melt. However, more recent results indicate that significant melting/sintering can occur before initial deformation is observed (Ref. 6). The fact that the time/temperature history of laboratory ash is quite different from conditions experienced in the boiler can result in difference in melting behavior. In addition, the ash used in this technique may not represent the composition of ash deposits that actually stick to the tube surfaces. Often there is a major discrepancy between the composition of as-fired ash and that which is found as deposits (See Table I). This is a major criticism of the ash fusibility temperatures. The discrepancies between fusibility temperature predictions and actual slagging performance is usually greater on ashes that may look reasonably good based on fusibility temperature results. One can usually assume, with reasonable confidence, that the melting temperature of the waterwall deposits will be no higher than ASTM fusibility temperatures; but deposit melting temperatures can be and are often lower than ASTM melting temperatures. This is because selective deposition of lower melting constituents can and does occur; hence there is an enrichment of lower melting material in the deposit.

Ash viscosity measurements suffer similar criticism to the fusibility measurements. These tests are conducted on laboratory ash and on a composite ash sample. Viscosity measurements are less subjective and more definitive than fluid temperature determination for the assessment of ash flow characteristics. However, these measurements reflect the properties of a totally dissolved solution of ash constituents and may not be representative of slag deposit properties in pulverized coal-fired boilers. During pulverized coal firing, a severe problem may already exist before slag deposits reach the fluid/running state. Generally, only a small quantity of liquid phase material exists in deposits and it is the particle-to-particle surface bonding which is most important.

Much use is made of the ash composition which is normally a compilation of the major elements in coal ash expressed as the oxide form. From this compilation of elements, expressed as oxides, judgements are often made based on the quantity of certain key constitutents like iron and sodium. Base/acid ratios are computed and used as indicators of ash behavior; normally lower melting ashes fall in the 0.4 to 0.6 range. It has been shown that base/acid ratios generally correlate with ash softening temperatures, so although base/acid ratios have helped explain why ash softening temperatures varied, it has not improved predictive capabilities in the authors' opinion. Other ratios such as Fe/Ca and Si/Al have been used as indicators of ash deposit behavior. Ratios like these have helped to explain deposit characteristics, but their use as a prime predictive tool is questionable especially since these ratios do not take into account selective deposition nor do they consider the total quantities of the constituents present. An Fe/Ca ratio of 2 could result from 6/3 or 30/15; the latter numbers would generally indicate a far worse situation than the former, but ratios don't show this.

Many slagging and fouling indices are based upon certain ash constituent ratios and corrected using such factors as geographical area, sulfur content, sodium content, etc. One commonly used slagging index uses Base/Acid ratio and sulfur content. Factoring in sulfur content is likely to improve the sensitivity of this index to the influence of pyrite on slagging. (As previously discussed, iron-rich minerals often play an important role in slagging.) However, the use of such "correction" factors is often a crude substitute for more detailed knowledge of the fundamental fuel properties. Another example of this is the use of chlorine content in a coal as a fouling index. This can be true if the chlorine is present as NaCl thereby indicating the concentration of sodium which is in an active form and that will, in fact, cause the fouling. Chlorine present in other forms may or may not adversely affect fouling.

Sintering strength tests have been used as an indication of fouling potential. Assuming that correct ash compositions have been represented (which is less of a problem in the convection section than in the radiant section) worthwhile information may be obtained relative to a time/temperature vs. bonding strength relationship. In order for sintering tests to accurately predict actual behavior it is necessary that tests be conducted with ash produced under representative furnace conditions (time-temperature history). Fouling behavior is often greatly influenced by sodium reactions. Sodium which vaporizes in the furnace can condense in downstream convection sections thereby concentrating on flyash surfaces. Particle surface reactions are primarily responsible for convection deposit bonding.

In summary, traditional methods for prediction ash deposit characteristics are heavily based upon ash chemistry. These convectional analyses do not provide definitive information concerning the mineral forms present in the coals and the distribution of inorganic species within the coal matrix. Such information can be extremely important in extrapolating previous experience, since the nature in which the inorganic constituents are contained in the coal can be the determining factor in their behavior during the ash deposition process.

ASSESSMENT OF NEW PREDICTIVE TECHNIQUES

Generally speaking the newer bench scale predictive techniques are far more sensitive to the conditions that exist in commercial furnaces than the older predictive methods. Selective deposition, for example, has been recognized as a phenomenon which cannot be ignored. More attention is being paid to fundamentals of the ash formation and deposition processes. New tools, such as Scanning Electron Microscopy (SEM), are being considered as ways to improve predictive capabilities. Other, more specialized bench scale apparatuses are being developed to simulate important aspects of commercial conditions and provide quantitative information on parameters that influence bonding strength.

Recent work has shown that pulverized coal, if separated by gravity fractionation, can yield important information relative to slagging potential due to the iron content. (Ref. 6, 7). Results of this work have shown that the percentage of iron in the heavy fractions correlates very well to the slagging behavior in commercial boilers. (See Figure 3). This technique appears to identify the proportion of relatively pure pyrites particles that are generated in the pulverized coal feed and that are capable of melting at relatively low temperatures and that would account for enrichment of iron in lower furnace waterwall deposits.

A method for measuring active alkalies has been developed as a means for improved prediction of fouling potential (Ref. 8). Previous wisdom held that fouling potential was directly related to the total sodium content. Much of this early work was done on low rank coals in which case it was not uncommon for all of the alkalies to be present as an active sodium form (Ref. 9). However, there were many occasions where the fouling potential was not adequately predicted by the total sodium content. (Table II provides some examples of anomalous fouling behavior.) The mechanism postulated for sodium-related fouling was one of a vaporization/condensation mechanism. Simple forms of sodium compounds resulted in the vaporization of sodium in the radiant zone of the furnace where peak temperatures are generated. Subsequent condensation of the sodium on the relatively cool tube surfaces effected a process for deposition of sodium. Sodium is a known, effective fluxing agent that can create hard, bonded deposits. The referenced method relied on the use of weak acid to preferentially leach out sodium from simple compounds like NaCl and/or organically-bound alkali as would be present in many of the lower rank coals. This method gives results that correlate well with field performance on coals having significant sodium contents (See Table II).

The use of new analytical techniques promises to give results that allow mineral matter to be identified according to composition, mineral form, distribution within the coal matrix, and grain size.

Techniques such as computer-controlled scanning electron microscopy (CCSCM) transmission electron microscopy (STEM), X-ray diffracton can be used to characterize these properties on individual particle by particle basis. New spectroscopies such as extended X-ray absorption of fine structure spectroscopy (EXAFS), and electron energy loss spectroscope, (EELS) are capable of determining electronic bonding structure and local atomic environment for organically associated inorganics like calcium, sodium and sulfur. Other new techniques such as Fourier transform infrared spectroscopy (FTIR), electron microprobe, electron spectroscopy for chemical analysis (ESCA), etc. all provide methods of improving present capabilities. By development and application of these techniques a much better fundamental assessment of coal mineral matter behavior is possible. The authors believe these results, coupled with those of other existing methods, can make a significant improvement to predictive capabilities.

AREAS OF UNCERTAINTY

Prediction of ash deposit characteristics based solely on bench-scale fuel properties always requires substantial judgement and allows only a certain level of confidence. As discussed, the ash deposition process is so complex that detailed modelling of commercial systems based on fundamental data is presently unrealistic. However, current techniques can provide relative data which in most cases is sufficient to make accurate assessment of slagging and fouling potentials relative to other fuels.

There remains many areas of uncertainty where experienced judgements must fill the gap between good laboratory results/predictions and boiler design decisions. One of these areas concerns the extent of deposit coverage in a boiler. Though the fuels researcher may adequately characterize a given coal ash in terms of its potential deposit effects, he is often at a loss to adequately describe the extent of coverage of deposits in the boiler. It is necessary to accurately describe furnace conditions in order to assess resulting deposits in particular boiler regions. Though some good work is underway in this area, the question of bonding strength and cleanability remains a problem as far as its prediction from bench scale tests. Though some good correlations have been developed between iron content of heavy gravity fractions and slagging, there does not exist a bench scale technique that can simulate what the ash deposit composition shall be when burned in a commercial boiler.

It is possible to increase the level of confidence for prediction of deposit effects by conducting pilot-scale combustion studies in test rigs which more closely simulate the conditions present in commercial boilers. Combustion testing allows evaluation of the ash formation and deposition process and permits detailed characterization of deposits generated. Results can allow determination of deposit characteristics as a function of fundamental boiler design parameters (such as gas temperature, velocity, etc.). Combustion test rigs also serve as valuable tools for assessment of fuels with very unusual properties and can significantly reduce uncertainties in extrapolation of their behavior from past experience.

Whenever test results are assessed and used to establish boiler design parameters, the representativeness of the test sample must be carefully considered. The degree of variability in the coal deposit and its impact on the day-to-day fuel properties

are very important factors which must be evaluated. Judgements are also required on long term coal supply properties.

In summary, it can be stated that the ash formation and deposition process is not fully understood. Traditional ASTM analyses do not always provide information that can be used to make predictive judgements at the confidence levels desired. Newer techniques have been developed and are being developed that are more sensitive to the conditions that exist in the boiler environment, and that recognize the heterogeneity of the inorganic constituents in the coal matrix. There appears to be a recognition that no one test can adequately describe coal ash behavior; a combination of tests, each designed to focus on a particular aspect of ash behavior seems to be a logical approach. Based on the results from many of these newer tests, on coals that are presently being burned in existing units, the authors feel certain that significant improvements have been made in predicting ash behavior. Finally the authors suggest that attention be given, by cognizant people, to the idea of standardizing some of the newer predictive techniques and incorporating them as supplements to existing ASTM tests.

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FIGURE 1

EFFECT OF COAL PROPERTIES ON FURNACE SIZE

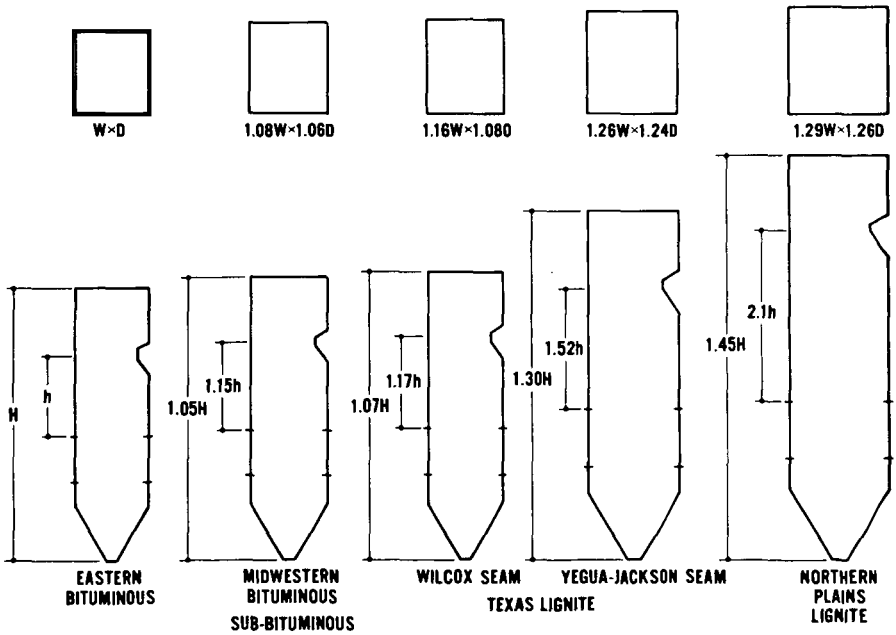

FIGURE 2

SUPERHEATER DEPOSIT BUILDUP vs FLUE GAS TEMPERATURE

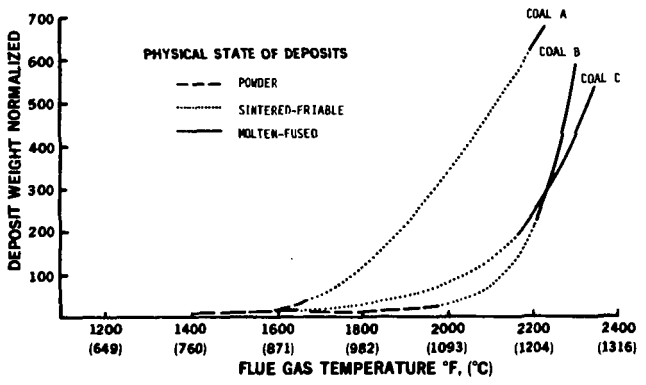

FIGURE 3

EFFECT OF SEGREGATED IRON ON COAL ASH SLAGGING
SLAGGING POTENTIAL
VERSUS
PERCENT IRON IN 2.9 GRAVITY FRACTION

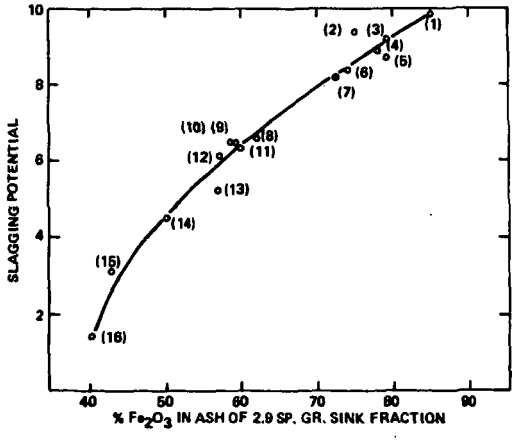

TABLE I

ENRICHMENT OF IRON IN BOILER WALL DEPOSITS
COMPARISON OF COMPOSITION OF ASH
DEPOSITS AND AS-FIRED COAL ASHES

UNIT	1		2		3	
SAMPLE	AS-FIRED COAL ASH	WATERWALL DEPOSIT	AS-FIRED COAL ASH	WATERWALL DEPOSIT	AS-FIRED COAL ASH	WATERWALL DEPOSIT
Ash Composition						
SiO_2	47.0	33.3	50.2	55.1	49.7	41.8
Al_2O_3	26.7	18.0	16.9	14.6	16.5	15.8
Fe_2O_3	14.6	43.5	5.9	18.3	12.0	28.5
CaO	2.2	1.2	12.8	7.2	6.5	9.0
MgO	0.7	0.5	3.5	2.0	0.9	0.9
Na_2O	0.4	0.2	0.6	0.5	1.1	0.6
K_2O	2.3	1.6	0.8	0.6	1.5	0.9
TiO_2	1.3	0.8	0.9	0.8	1.1	0.7
SO_3	1.1	0.5	12.0	0.1	2.0	0.2

TABLE 2 **ANALYTICAL DATA ON U.S. COALS**

Rank Region	**Lignite N. Dakota**	**Sub B Montana**	**Lignite Texas (Yegua)**	**Lignite Texas (Wilcox)**	**hvBb Utah**	**hvAb Penn**	**Lignite Texas (Wilcox)**
(Dry Basis)							
Volatile	44.4	42.2	39.6	41.0	41.5	32.5	38.1
Fixed C	46.0	52.0	26.9	39.5	48.3	54.0	33.0
Ash	9.6	5.6	33.5	19.5	10.2	13.5	28.9
HHV (Btu/lb) (Dry Basis)	10640	12130	7750	9710	12870	13200	8420
Ash Fusibility							
I.D. (°F)	2130	1980	1940	2150	2190	2370	2210
S.T.	2180	2020	2200	2250	2270	2510	2300
H.T.	2190	2060	2430	2340	2390	2560	2420
F.T.	2200	2170	2610	2530	2620	2660	2620
Ash Composition							
SiO_2 (%)	20.0	33.9	62.1	52.3	52.5	51.1	57.9
Al_2O_3	9.1	11.4	15.1	17.4	18.9	30.7	21.8
Fe_2O_3	10.3	10.8	3.5	5.3	1.1	10.0	3.9
CaO	22.4	21.0	6.2	9.4	13.2	1.6	7.1
MgO	6.4	2.7	0.7	3.2	1.3	0.9	2.1
Na_2O	5.0	5.8	3.6	0.9	3.8	0.4	0.9
K_2O	0.5	1.6	2.1	1.2	0.9	1.7	0.8
TiO	0.4	0.7	0.9	1.2	1.2	2.0	1.1
SO_3	21.9	12.0	6.1	9.6	6.2	1.4	4.4
Total alkali, %, ash basis							
Na_2O	5.0	5.8	3.6	0.9	3.8	0.4	0.7
K_2O	0.5	1.6	1.9	1.2	0.9	1.7	0.8
Soluble Alkali, %, ash basis							
Na_2O	5.58	6.45	3.88	0.71	1.49	0.15	0.16
K_2O	—	—	0.44	0.04	0.08	—	0.05
Relative Soluble Alkali, %							
Na_2O	112%	111%	108%	79%	39%	38%	23%
K_2O	—	—	—	3%	9%	—	6%
Fouling Potential	**Severe**	**High**	**High**	**Moderate**	**Moderate**	**Low**	**Low**